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<b>(21) International Application Number:</b> PCT/EP95/00615 <b>(22) International Filing Date:</b> 21 February 1995 (21.02.95)  <b>(30) Priority Data:</b> MI94A000408 7 March 1994 (07.03.94) IT  <b>(71) Applicant:</b> PPG INDUSTRIES ITALIA S.R.L. [IT/IT]; Via Genova, 31, I-12010 Fraz. Spinetta (IT).  <b>(72) Inventors:</b> FERRARI, Giancarlo; Via Trieste, 18/3, I-15028 Quattordio (IT). PANFILI, Mario; Via Galvani, 31, I-15100 Alessandria (IT). TOMALINO, Massimo; Via Petrarca, 1, I-14100 Asti (IT).  <b>(74) Agents:</b> VANNINI, Torquato et al.; Jacobacci & Perani, Via Visconti di Modrone, 7, I-20122 Milano (IT).		<b>(81) Designated States:</b> BR, CN, MX, PL, RO, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> AN ADHESIVE COMPOSITION FOR FILLING BOX PARTS OF VEHICLE BODIES  <b>(57) Abstract</b>  An adhesive composition for filling box parts of vehicle bodies includes from 20 to 35 % of PVC resin (PVC/PVA) and from 5 to 15 % of a hot-expanding agent constituted by an acrylonitrile/acrylic ester/olefin copolymer, encapsulating an appropriate quantity of a C <sub>4</sub> -C <sub>6</sub> alkane.		

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"AN ADHESIVE COMPOSITION FOR FILLING BOX PARTS OF  
VEHICLE BODIES"

The present invention relates generally to the filling  
5 of "box parts" of vehicle bodies.

The term "box parts", in the technical jargon of this  
field, means parts of vehicle bodies which are hollow.

10 More particularly, this invention relates to a  
polymeric composition for filling hollow box parts of  
vehicle bodies.

It is known that vehicle bodies include a certain  
15 number of box parts. It is also known that the  
presence of these box parts is a problem due to the  
fact that, being hollow, they propagate and amplify  
vibrations.

20 Moreover the cavities in these box parts tend to  
collect moisture and thus constitute zones in which the  
body is particularly prone to corrosion.

It is therefore necessary to fill these box parts in  
25 order to achieve effective sound-proofing and  
protection against corrosion. In the prior art, these  
box parts have usually been filled by the injection  
thereinto of compositions based respectively on a polyol

resin and an isocyanate which, on mixing, react at ambient temperature or on heating during the passage of the body through bodywork or painting ovens, thus polymerising and forming a polyurethane foam. The  
5 considerable increase in volume which occurs during the formation of the foam enables the box part to be filled completely. This achieves soundproofing and protection against corrosion.

10 The use of the above resins is not, however, free from problems from the point of view of economics and, more particularly, from environmental and toxicological viewpoints.

15 In practice, the two compositions which must be mixed to give the polyurethane foam are housed in small cylinders or in large pressurised containers; in the first case only 60% of the total contents of the cylinder can be supplied and the cylinder, still containing a  
20 considerable quantity of the product, must then be sent for disposal which can be carried out only by specialist firms.

In the second case the pressurised containers, after  
25 emptying, which again in this case is only partial, must be cleaned thoroughly before being refilled.

In both cases the environmental and economic problems

resulting from the use of such polyurethane foams will be evident.

5 Finally, due to the fact that the components of polyurethane foams are extremely toxic, it is necessary to take extremely rigorous safety precautions in equipping the workforce who handle them, which workforce must wear bulky and uncomfortable protective clothing if not actual pressure suits.

10

As a result of the problems listed above, vehicle manufacturers have put a great deal of effort into research to identify alternative methods of solving the problem of filling box parts of vehicle bodies.

15

Among the solutions proposed as alternatives to the use of polyurethane foam may be mentioned the use of pre-formed materials based on rubbers or derivatives of ethyl vinyl acetate (EVA) which, formed into suitable shapes and sizes, are introduced into the body parts before the bodywork or painting stages. During the heating which occurs in these stages, these materials expand to fill the entirety of the box parts.

20

25 These materials perform just as well as polyurethane foams at providing sound proofing and protection against corrosion, particularly when pre-formed articles anchored to metal bases are used since, in such cases, it is

possible for them to be fitted precisely into the box space by welding of the metal base to the box wall.

5 The use of such pre-formed materials clearly avoids the environmental and toxicological problems connected with the use of polyurethane foams but at considerable expense because of the high cost of the materials themselves and because of the labour intensity of their application which adds to the costs of their use.

10

The problem at the root of the present invention is that of providing a composition which is suitable for filling box parts of motor vehicle bodies and which avoids the problems of the prior art indicated above, that is, which  
15 does not give toxicological and environmental problems and is easy and economic to put into practice.

This problem is solved according to the invention by an adhesive composition for filling box parts of motor  
20 vehicle bodies, including, in percentages by weight of the weight of the composition, from 20 to 35% of PVC resin (PVC/PVA), characterised in that it includes from 5 to 15% of a hot-expanding agent, constituted by an acrylonitrile/acrylic ester/olefin copolymer,  
25 encapsulating an appropriate quantity of a C<sub>4</sub>-C<sub>6</sub> alkane.

In a preferred embodiment, the hot-expanding agent is used in the form of microspheres of the copolymer

incorporating a C<sub>4</sub>-C<sub>6</sub> alkane and having a diameter of 8-15 microns.

The C<sub>4</sub>-C<sub>6</sub> alkane is preferably isobutane.

5

The hot-expanding agent used is preferably the material sold under the name EXPANCEL by EXPANCEL NOBEL INDUSTRIES SWEDEN.

10 To advantage the adhesive composition also includes from 0.5 to 1.5% of a low-density filler.

Preferably the low-density filler is constituted by a pre-expanded acrylonitrile/acrylic ester/olefin copolymer  
15 encapsulating an appropriate quantity of a C<sub>4</sub>-C<sub>6</sub> alkane.

A preferred adhesive composition for filling box parts of motor vehicle bodies in general comprises, in percentages by weight of the total weight of the composition:

20

Resin PVC(PVA)	23-32
Plasticisers	27-37
Adhesion promoters	1-10
Natural and/or coated fillers	25-35
25 Hot-expanding agent	5-15
Low-density filler	0.5-1.5
Additives and pigments	2-6
Catalysts and accelerators	0-1

A plasticiser which is useful for the purposes of the present invention is selected from the group comprising phthalates, adipates, benzoates, trimellitates, sulphonates and their mixtures.

5

The mineral fillers, which may be natural and/or coated, are those commonly used in known formulations for adhesives for vehicle bodies and include calcium silicates and carbonates, talc, mica, kaolin, titanium dioxide and the like.

10

Among the adhesion promoters used for the purposes of the present invention may be mentioned those selected from the group comprising polyamine - polyamide resins, epoxy resins, melamine resins, polyurethane resins and ureic resins.

15

The low-density filler preferably used is a pre-expanded copolymer sold by EXPANCEL NOBEL INDUSTRIES SWEDEN under the name EXPANCEL.

20

The catalysts and accelerators which are most useful are polyamines, peroxides, amides and the like.

25

All the formulations of the composition of the invention which fall within the values specified above can be applied extremely well with the use of techniques and apparatus currently used for prior-art adhesive



compositions.

More particularly, the material of the invention may be applied to box parts of vehicle bodies with the use of airless pumps with a 45:1 compression ratio and spray guns with extrusion nozzles, that is, adapted to enable the correct outflow of materials with an average-high viscosity (300,000 - 800,000 cps).

The application may be carried out during the bodywork phase, the composition of the invention being deposited directly on to the metal surface of the body before the cataphoretic painting and subsequent baking at 150-180°C.

Alternatively the composition of the invention may be applied to the cataphoretically polymerised paint and subsequently baked at a temperature of 140-160°C.

The thickness of the composition layer advisable to achieve satisfactory filling of the box parts may vary very widely according to the geometric characteristics and volume of the box; in general, the optimum quantity, and hence thickness, of material should be regulated to take account of the expansion ratio of the material itself in dependence on the baking cycle to which it is to be subject.

To obtain uniform application it is advisable to supply

the composition of the invention at a temperature of between 20 and 25°C.

5 The optimum heat-transformation is achieved with a baking period of about 30 minutes, with a temperature range of between 140 and 180°C.

At the end of the baking period, the adhesive composition of the present invention fills the box parts  
10 completely, being in contact with and adhering to their walls and forming a complete seal while retaining a compact, microcellular, and hence low-density, structure. As a result of these properties, extremely good performance is achieved as regards sound insulation and  
15 protection against corrosion.

It is worth the trouble to stress the fact that the adhesive composition of the invention is a material that is toxicologically and ecologically sound in that, unlike  
20 polyurethane foams, it does not contain nor give off toxic and noxious substances during any phase in its use (application or baking) and does not present any problems for disposal.

25 Furthermore, the composition of the invention is very easy to apply, its application being possible with the equipment commonly used in production lines by all motor vehicle manufacturers for the extrusion of adhesives and

sealants. This ease of application gives the advantage that considerable labour savings may be made compared with the use of methods involving the application of pre-formed materials.

5

The ease of application of the composition of the invention is such that it may realistically be robotised, with consequent further advantages from the point of view of saving on labour and production times.

10

Further characteristics and advantages of the invention will become clearer from several examples of adhesive compositions for filling bodywork box parts and from the results of tests carried out on them, given below, purely by a way of non-limitative example, and in which all the parts and percentages are given by weight of the total weight of the composition if not otherwise indicated.

20

#### EXAMPLE 1

The following components were measured successively into a horizontal mixer provided with a stainless-steel stirrer rotated at 17-25 revolutions per minute:

25

Plasticisers	37
Adhesion promoters	1
Additives and pigments	5.5

Stirring was continued out for 10 minutes to achieve homogenous mixing and the following components were then added to the mixture:

	Microspherical expanding agent (EXPANCEL)	5
5	Vinyl resin	24
	Low-density filler (pre-expanded EXPANCEL)	1.5
	Natural and coated fillers	26

After further stirring for about 10 minutes the mixture  
10 was perfectly homogenous.

The composition obtained was applied by a painting technique to the metal surface of a bodywork box part already coated with electrophoretic paint, the part  
15 corresponding to a front structural member of a motor vehicle (model Lancia Thema), with the use of about 500 grams of the product.

The application was carried out at an ambient temperature  
20 of 22°C.

After baking in an oven at 145°C for 25 minutes, the product had expanded so as to fill the box part completely.  
25

## EXAMPLE 2

The same procedure as in Example 1 was carried out with the use of the same components to obtain a composition  
5 which included 10% of the hot expanding agent (EXPANCEL) and 1.0% of the low-density filler (pre-expanded EXPANCEL).

The composition was easily applied by the prior-art  
10 apparatus and equipment in the same layout.

## EXAMPLE 3

The procedure of Example 1 was repeated with the same  
15 components with the exception that 15.0% of the expanding agent (EXPANCEL) and 0.5% of low-density filler (pre-expanded EXPANCEL) were used.

The application was carried out in a manner described in  
20 Example 1.

The standard tests normally used by motor-vehicle manufacturers to evaluate the soundproofing qualities of materials used to fill the box parts of the motor vehicle  
25 bodies were carried out on the adhesive compositions obtained in the preceding examples.

The results of these tests are given in the table below.

TABLE

	EXAMPLE 1	EXAMPLE 2	EXAMPLE 3
Brookfield Viscosity (cps)	550000	530000	530000
5 Extrusion (sec)	60	60	39
Density (g/cc)	0.800	0.903	1.063
Expansion ratio	1:3	1:8	1:13
Apparent density (g/cc)	0.1990	0.0872	0.0665
10 Absorption of water (%)	< 5	< 5	< 5
Adhesion	OK	OK	OK
Resistance to corrosion	OK	OK	OK
15 Sound-proofing	OK	OK	OK

Of the data given above, those relating to the absorption of water and resistance to corrosion should be considered particularly since these are crucial if one of the more important objects of the present invention, that is, protection of the box parts against corrosion is to be achieved.

The data are completely satisfactory and it is thought that this can be attributed to the expanded structure of the adhesive at the end of its application and baking. In fact, the expanded structure of the adhesive includes a plurality of spheroidal cells of very regular diameter, very uniformly distributed throughout the thickness of the filling constituted by the adhesive.

Each cell is constituted by a sheath of acrylonitrile/acrylic ester/olefin copolymer encapsulating C<sub>4</sub>-C<sub>6</sub> alkane.

- 5 The expanded structure of the filling constituted by the adhesive is not porous however since it is not created by substances which liberate gas due to the heat treatment, giving rise to pores which are very different from each other and irregularly distributed and which form cavities
- 10 in which moisture may collect.

## CLAIMS

1. An adhesive composition for filling box parts of motor-vehicle bodies, including, in percentages by weight  
5 of the weight of the composition, from 20 to 35% of PVC resin (PVC/PVA), characterised in that it includes from 5 to 15% of a hot-expanding agent constituted by an acrylonitrile/acrylic ester/olefin copolymer, encapsulating an appropriate quantity of a C<sub>4</sub>-C<sub>6</sub> alkane.  
10
2. A composition according to Claim 1, characterised in that the copolymer incorporating C<sub>4</sub>-C<sub>6</sub> alkane is used in the form of microspheres having a diameter of 8-15 microns.  
15
3. A composition according to Claim 2, characterised in that the C<sub>4</sub>-C<sub>6</sub> alkane is isobutane.
4. A composition according to Claim 3, characterised in  
20 that it includes from 0.5% to 1.5% by weight of the weight of the composition of a low-density filler.
5. A composition according to Claim 4, characterised in that the low-density filler is a pre-expanded  
25 acrylonitrile/acrylic ester/olefin copolymer encapsulating an appropriate quantity of C<sub>4</sub>-C<sub>6</sub> alkane.
6. An adhesive composition for filling box parts of



15

motor-vehicle bodies, characterised in that it includes, in percentages by weight of the total weight of the composition:

5	Resin PVC(PVA)	23-32
	Plasticisers	27-37
	Adhesion promoters	1-10
	Natural and/or coated fillers	25-35
	Hot-expanding agent	5-15
10	Low-density filler	0.5-1.5
	Additives and pigments	2-6
	Catalysts and accelerators	0-1

7. A composition according to Claim 6, characterised in  
15 that the hot-expanding agent is constituted by an  
acrylonitrile/acrylic ester/olefin copolymer,  
encapsulating an appropriate quantity of a C<sub>4</sub>-C<sub>6</sub> alkane  
and the low-density filler is a pre-expanded  
acrylonitrile/acrylic ester/olefin copolymer  
20 encapsulating an appropriate quantity of a C<sub>4</sub>-C<sub>6</sub> alkane.

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08J9/32 C09J5/08 C09J127/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO,A,94 22967 (PPG INDUSTRIES ITALIA S. R. L.) 13 October 1994 see the whole document -----	1-7

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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